

# About Modification of the Physical Properties of Lead Selenide under the Ir-Laser Radiation Treatment

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**Abstract – Physical properties of PbSe single crystal samples, both undoped and doped with manganese and europium, have been studied. In the transmission region ( $\hbar\omega < E_g$ ) the laser light changes the carrier density and mobility. It also changes the distribution of intrinsic and extrinsic components among lattice sites. The donor level in the band gap ( $E_d = -0.05$  eV), which is manifested in the illuminated crystals, does not depend on the type of dopant. It belongs to intrinsic defects.**

## 1. Introduction

Impurity states have attracted close interest in research on IV–VI semiconductor compounds for many years now [1]. The interest stems from the extensive practical use of these compounds as IR optoelectronic devices and thermoelectric generators and also from the unusual behavior of impurities and intrinsic defects, which actively influence the effectiveness of devices based on these compounds.

This research has gone into most detail on the behavior of group – III impurities of the periodic table in IV–VI compounds. Impurities of this group have substantial effects on the electrical properties, the mechanisms for the scattering of current carriers, and the structure of the energy spectrum. Nevertheless, the doping mechanism, the positions of the impurities in the lattice, and the charge states of the impurities are still largely in the realm of assumptions and require detailed research.

Several experiments [2, 3] have shown that in the course of doping from the melt, even at a low impurity concentration  $N_i \approx 1.0 \cdot 10^{19} \text{ cm}^{-3}$ , there is a tendency toward the formation of large-scale defects containing intrinsic and impurity metallic components, which are manifested in the optical and electrical properties of the corresponding crystals [3, 4]. If these factors are ignored, one may draw distorted conclusions regarding the nature of the energy spectrum of the impurity states.

It was shown in Refs. [3–6] that the application of IR laser light in the transmission region of the crystal matrix ( $\hbar\omega < E_g$ ) of PbSnTe crystals, which either are undoped or have a relatively low impurity concentration  $N_i \approx (1-2) \cdot 10^{19} \text{ cm}^{-3}$ , has the consequence that the impurity atoms and the intrinsic atoms diffusing away from inclusions and interstitial positions occupy

sites of the metal sublattice, thereby altering the concentration of free carriers and their mobility.

In this paper we are reporting a study of the electrical properties and electron spin resonance (ESR) of PbSe single crystals, both undoped and doped with manganese and europium. We have also studied the changes caused in these properties by IR laser light. The use of transition elements and rare-earth elements as impurities makes it possible to follow the laser-stimulated modification of the bulk properties crystals at the atomic and to obtain information on the doping mechanism and charge state of the impurity.

## 2. Samples and their Electrical Properties

The PbSe:(Mn, Eu) single crystals were grown by directed crystallization from the melt. The impurity concentration was varied over the range  $N_i \approx 5 \cdot 10^{17} \div 2 \cdot 10^{19} \text{ cm}^{-3}$ . The samples of a first lot had a p-type conductivity (regardless of the manganese and europium concentrations); at 77 K they had a concentration  $P = (2 \div 20) \cdot 10^{18} \text{ cm}^{-3}$  and a carrier mobility  $\mu = 2 \cdot 10^3 \div 1.2 \cdot 10^4 \text{ cm}^2/(\text{V} \cdot \text{s})$ . Undoped PbSe crystals have the same electrical properties. A second lot of doped samples were characterized by an anomalous conductivity inversion and a low carrier mobility [ $\mu = 10^2 \text{ cm}^2/(\text{V} \cdot \text{s})$  at  $T = 77 \text{ K}$ ].

The crystals were exposed to IR light at  $\hbar\omega < E_g$  ( $E_g$  is the width of the  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  band gap at 300 K). The power density  $W$  of the laser light was below threshold at which the crystal would melt. The temperature of the samples in the course of the illumination was held well below the temperatures required for the thermal transformation of defects.

Figure 1 shows a typical curve of the hole concentration ( $T = 77 \text{ K}$ ) for PbSe, PbSe:(Mn, Eu) single crystals versus the illumination time  $t$  at a constant laser power density. At illumination times  $t \leq 5 \text{ h}$ , the hole density decreases; then the type of conductivity changes, and the electron density increases (region I in Fig. 1). The laser-stimulated changes in the carrier density then change direction: The electron density falls off (regions II and III in Fig. 1), and at electron density  $N = 1.26 \cdot 10^{18} \text{ cm}^{-3}$  ( $T = 77 \text{ K}$ ) there is essentially no dependence on the illumination time (at  $W = 25 \text{ W/cm}^2$ ). The mobility increases to  $3.86 \cdot 10^4 \text{ cm}^2/(\text{V} \cdot \text{s})$  and then varies only negligibly during the illumination.

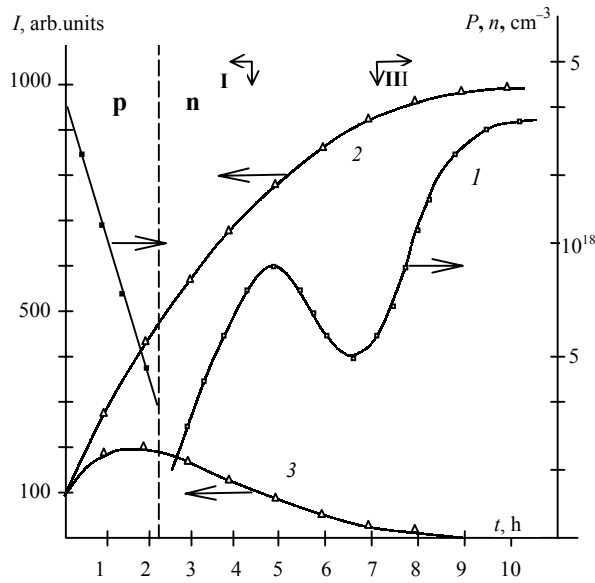


Fig. 1. The hole concentration ( $P, n$ ) at  $T = 77$  K (1) and intensity of the ESR line ( $I$ ) at  $T = 20$  K (2, 3) versus the illumination time for a PbSe : Mn single crystal. 2 –  $Mn^{2+}$  in lattice site; 3 –  $Mn^{2+}$  in interstitial position ( $W = 25$  W/cm<sup>2</sup>)

In the  $Pb_{0.93}Sn_{0.07}Se$  crystals, the dependence of the carrier density on the illumination time and on the laser power density is clearly of a unipolar nature, as in the  $Pb_{1-x}Sn_xTe$  ( $0 \leq x \leq 0.23$ ) solid solutions [5, 6]. It corresponds to  $P, N(t, W)$  for lead selenide (region I in Fig. 1). As the laser power density is raised, the rate of the laser-stimulated change in the carrier density increases in PbSnSe, as it does in PbSnTe (Fig. 2). As a result, regions I, II and III (for PbSe) shift toward shorter illumination times and toward lower electron densities in the saturation region.

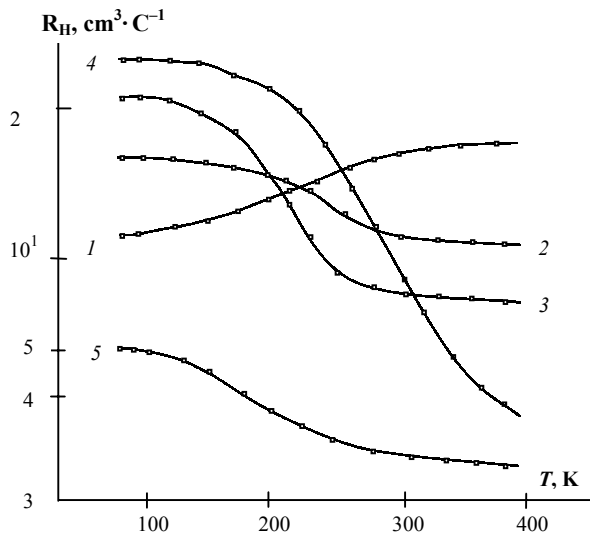


Fig. 2. Temperature dependence of the Hall coefficient in samples (1) before and (2–5) after illumination. Test samples: 1 – p-PbSe; 2 – p-PbSe; 3, 4, 5 – n-PbSe

At the power density  $W \approx 10$  W/cm<sup>2</sup>, we do not observe transitions to regions II and III at all. We should also point out that the time required to reach a

particular type of conductivity also depends on the original density of free carriers. Similar results were found for the second lot of crystals, in which the changes in the electrical properties were even more noticeable.

The laser-stimulated changes in the electrical properties are of a bulk nature, as can be seen from the changes in the optical transmission in accordance with the changes in the density of free carriers.

The temperature dependence of the Hall coefficient,  $R_H(T)$ , of lead selenide is shown in Fig. 2 for a constant laser power density and various illumination times. The curve of  $R_H(T)$  (curve 1 in Fig. 2) for PbSe doped with manganese and europium is characteristic of p-PbSe and has no structural features associated with the dopant. After the laser-stimulated change in conductivity type, the  $R_H(T)$  curve acquires a region associated with ionization of a level  $E_d$ , localized in the band gap (curves 3–5 in Fig. 2). Here the electron density is given by

$$n(T) = n_0 + \left( \frac{2m_d}{h^2} \right)^{\frac{3}{2}} \cdot \frac{(kT)^{\frac{3}{2}}}{3\pi^2} \cdot ({}^0L_0)^{\frac{3}{2}},$$

where  $({}^0L_0)^{\frac{3}{2}}$  are two parameter Fermi integrals,  $m_d$  is the effective mass of the density of states in the conduction band, and  $n_0$  is the electron density at 0 K. The energies are reckoned from the bottom of the conduction band.

The solid curves in Fig. 2 show the temperature dependence of the Hall coefficient,  $R_H(T)$ , calculated in this model. The energy position of the level in the band gap varies linearly with the temperature:  $E_d(T) = E_d(0) + 1.3 \cdot 10^4 T$  eV, where  $E_d(0) = -0.05$  eV is the activation energy for the level at  $T = 0$  K.

In the  $Pb_{0.93}Sn_{0.07}Se$  solid solutions,  $E_d$  is not manifested on the curve of  $R_H(T)$  in the region of the n-type conductivity, apparently because at  $x = 0.07$  this level is near the bottom of the conduction band ( $\Delta E \cong kT$ ).

The behavior of  $R_H(T)$  for n-PbSe and n-PbSe:(Mn; Eu) implies the structural features observed are not due to the impurity and are instead due to intrinsic defects.

Analysis of  $R_H(T)$  shows that with increasing illumination does, the density of states at the  $E_d$  level in the band gap decreases from  $8 \cdot 10^{17}$  to  $1.2 \cdot 10^{17}$  cm<sup>-3</sup>. We believe that the reason for this decrease is a decrease in the concentration of point defects of a donor type, which do not belong to lead vacancies [7]. This interpretation is supported by the ESR results. Accordingly, we find it most likely that the donor level  $E_d$  in the band gap is associated with selenium vacancies or lead atoms in interstitial positions.

### 3. ESR Spectra and Discussion of Results

The ESR of the PbSe: Mn(Eu) single crystals was carried out on a VARIAN E-12 apparatus in the 3-cm wavelength range and the temperatures of 20–300 K.

In the PbSe: Mn crystals not exposed to the laser light, we observe six isotropic hyperfine-structure lines with the half-width  $\Delta H = 13$  Oe (lead selenide crystallizes in a cubic lattice of the NaCl type, with space group  $Fm\bar{3}m - ^5O_h$ ), which stem from an interaction of  $3d^5$  electrons of  $Mn^{2+}$  with the intrinsic nuclear moment  $I = 5/2$  of the  $^{55}Mn$  isotope, which are characteristic of single manganese ions (Fig. 3). In this case the constants of the spin Hamiltonian had the following values:  $g = 2.0003 \pm 0.0005$  and  $A = (65.95 \pm 0.2) \cdot 10^{-4} \text{cm}^{-1}$ , where  $A$  is the hyperfine structure constant.

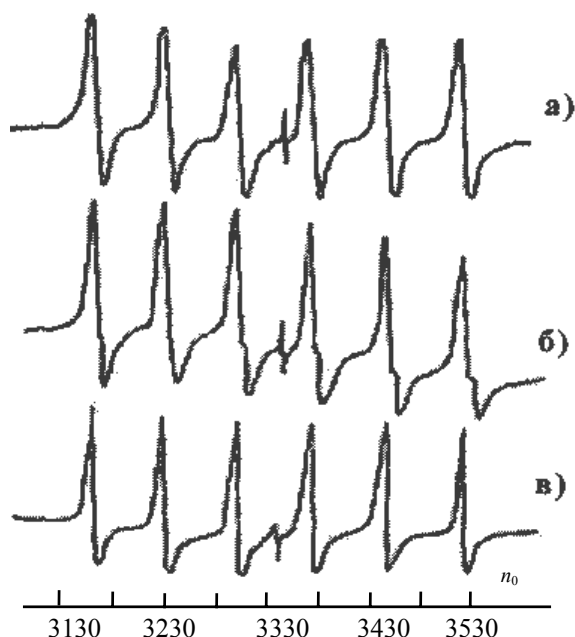


Fig. 3. ESR spectrum of  $Mn^{2+}$  in PbSe: Mn ( $T = 20$  K): a) before IR-laser irradiation; b) after 1 h irradiation; B) after 8 h irradiation ( $W = 25 \text{ W/cm}^2$ )

In the course of the illumination of the crystals, the total intensity of single ESR lines increases by more than an order of magnitude. This increase corresponds to an increase in the concentration of single  $Mn^{2+}$  ions. In addition, six more isotropic lines appear in ESR spectra. The intensity of the first sextet of lines initially increases slightly and then remains essentially constant up to the point at which the conductivity changes sign (Fig. 1). In the region of n-type conductivity, the intensity of these ESR lines decreases, and we do not observe the additional sextet against the background of the intense lines as the illumination time is raised. The constants of the spin Hamiltonian for the additional six lines were as follows:  $g = 1.9949 \pm 0.0005$  and  $A = (66.14 \pm 0.2) \cdot 10^{-4} \text{cm}^{-1}$ .

It should be pointed out that the half-width  $\Delta H$  of the hyperfine structure lines then decreased considerably ( $\Delta H = 8.5$  Oe).

At a fixed laser power density, the intensity of the additional ESR lines, like the carrier concentration,

reaches saturation as the illumination time is increased.

The appearance of the additional sextet of isotropic lines during the laser illumination of the crystals can be explained, as in the case of PbTe (Ref. 4), by the appearance of  $Mn^{2+}$  ions at lattice sites in the matrix of the PbSe crystal.

The results on the laser-stimulated changes in the bulk properties of the PbSe single crystals indicate that the mechanism for the interaction of the IR laser light with the crystal matrix is complicated and does not involve thermal processes.

The absence of the super-hyperfine interaction in the ESR spectra in the case of PbTe:Mn crystals [8] due to the interaction of the  $3d^5$  electrons of  $Mn^{2+}$  with the nuclear moments of the Se isotope ( $I = 1/2$ ) in the first coordination sphere could be explained by the fact that the nuclear moment of the Se isotope is 1.5 times smaller than the nuclear moment of the Te isotope. In addition, the half-width of the hyperfine structure lines in PbSe:Mn is considerably greater than in PbTe:Mn and the super-hyperfine constants satisfy the condition  $\alpha_{Se} < \alpha_{Te}$ , so that the super-hyperfine structure of PbSe:Mn cannot be resolved at  $T = 20$  K.

The same dependence of the intensity of an ESR line on the total illumination dose (or exposure dose) is observed in europium-doped lead selenide crystals.

The ESR spectrum of original samples PbSe:Eu was composed seven fine-structure lines of low intensity (corresponding to  $S = 7/2$ ), and each of them consisted of weakly resolved hyperfine structure lines.

The laser irradiation of PbSe:Eu increased considerably the intensity of the hyperfine structure lines and improved their resolution. The hyperfine structure was best resolved in the case of the strongest (due to the  $-1/2 \leftrightarrow +1/2$ ) central line in the spectrum. Away from the center of the spectrum, the intensity of the fine-structure lines fell (the ratio of the intensities of these lines observed on increase in the field amounted to approximately 3:33:10:93:10:33:3, although the theoretical ratio of the components of the fine-structure lines should be 7:15:12:16:12:15:7) and the hyperfine structure became less resolved. When a magnetic field with the orientation  $H \parallel \langle 100 \rangle$  ( $\Theta = 0$ ) was applied the solution of the fine-structure lines was the highest along the field scale.

The observed ESR spectrum of  $Eu^{2+}$  in PbSe was described satisfactorily by assuming the case of a strong magnetic field with the following transition frequencies [9]:

$$\begin{aligned} -1/2 \leftrightarrow +1/2 & \quad \hbar\omega = g \beta H_0, \\ \pm 7/2 \leftrightarrow \pm 5/2 & \quad \hbar\omega = g \beta H_0 \pm 20 b_4 p \pm 6 b_6 q, \\ \pm 5/2 \leftrightarrow \pm 3/2 & \quad \hbar\omega = g \beta H_0 \pm 10 b_4 p \pm 14 b_6 q, \\ \pm 3/2 \leftrightarrow \pm 1/2 & \quad \hbar\omega = g \beta H_0 \pm 12 b_4 p \pm 14 b_6 q, \end{aligned}$$

where  $p = 1 - 5 \Phi$ ,  $\Phi = \zeta^2 m^2 + m^2 n^2 + b^2 n^2$ ,  $q = 21/2 (11 \zeta^2 m^2 n^2 - \Phi + 2/21)$ , and  $\zeta$ ,  $m$ ,  $n$  are the direction cosines of the field  $H_0$  described in terms of the crystallographic axes.

The ESR spectrum obtained for  $H \parallel \langle 100 \rangle$  at  $T = 20$  K was used to find the constants of the spin Hamiltonian:  $g = 2.0231 \pm 0.0005$ ;  $b_4 = (92.8 \pm 2.0) \times 10^{-4} \text{ cm}^{-1}$ ;  $b_6 = (3.8 \pm 2.0) \cdot 10^{-4} \text{ cm}^{-1}$ ;  $A(^{153}\text{Eu}) = (29.0 \pm 0.2) \cdot 10^{-4} \text{ cm}^{-1}$ ;  $A(^{151}\text{Eu}) = (12.7 \pm 0.2) \cdot 10^{-4} \text{ cm}^{-1}$ .

It is well known that concentration supercooling in IV–VI compounds gives rise to regions enriched in the intrinsic metal and chalcogen components, and that as a result of doping these regions may acquire a wide spectrum of chemical compositions ranging from monatomic to quaternary compounds [10, 11]. Inhomogeneities of this type form potential barriers with the crystal matrix. These barriers cause an intense scattering of holes at low temperatures, as can be seen in the anomalous behavior of the mobility and Hall coefficient as function of the temperature. The presence of barriers is confirmed by the strong photo-emf signals in the absence of a bias voltage. The type of dopant determines the red boundary of this emf. In addition, interstitial atoms, which may be electrically active, are present in a substantial conservation in the crystal.

As the IR laser light interacts with the crystal, it leads to a dissociation of regions of this type and also to a diffusion of intrinsic and impurity ions in the field of the electromagnetic wave. At the beginning of the illumination (at  $t \leq 5$  h), the predominant process is a laser-stimulated filling of electrically active lead vacancies (acceptors) by the metal components: The hole densities fall off after the inversion of conductivity type, the electron density of selenium vacancies.

In the second stage of the illumination ( $5 \leq t \leq 7$  h) the process change direction: The electron density begins to decrease, but the change in  $N(t)$  with illumination time is slower than in the first stage of the illumination. In other words, a laser-stimulated filling of electrically active Se vacancies, which are doubly charged donors, becomes predominant. In the third stage ( $t \geq 8$  h), there is a sharp increase in the density of electrons, corresponding to an exclusion of a donor mechanism from the process (regions I and II in Fig. 1). This result is supported by the ESR results, which provide unambiguous evidence that the change in the carrier density in the region of n-type conducti-

vity cannot be attributed to changes in the metal sublattice of the lead selenide.

#### 4. Conclusion

In summary, it has been established that manganese and europium impurities in PbSe single crystals are distributed primarily among interstitial of the crystal lattice in the respective charge states  $\text{Mn}^{2+}$  and  $\text{Eu}^{2+}$ . They have essentially no effect on the carrier density ( $N_i \approx 2 \cdot 10^{19} \text{ cm}^{-3}$ ), and – like the intrinsic components – tend to form inclusions. The application of the IR laser light (at  $\hbar\omega < E_g$ ) leads to a distribution of intrinsic and impurity components (without changes in their charge state) among lattice sites and to changes in the carrier density.

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